

Correlation calculations for the reconstruction of the Si (100) surface

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Ab initio multi-reference configuration interaction calculations are performed for the Si(100) surface using a cluster approach. The convergence with respect to the cluster size is checked and the final results are taken from a $\text{Si}_{32}\text{H}_{28}$ cluster which models two dimers and six bulk layers. We find for the ideal as well as for the $p(1 \times 2)$ reconstruction a singlet ground state consisting of several configurations. The energy gain due to forming the symmetric dimer in the $p(1 \times 2)$ structure is 1.75 eV, the bond length of the dimer is 2.35 Å which is very close to the bulk value. In contradiction to the LDA results and in agreement with previous correlation calculations we do not find an asymmetric $p(1 \times 2)$ structure.

Keywords: Ab-initio quantum chemical methods and calculations; Surface relaxation and reconstruction; Silicon; Low index single crystal surface;

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I. INTRODUCTION

The Si(100) surface is one of the best examined, both experimentally¹⁻⁷ and theoretically⁸⁻¹⁹, semiconductor surfaces due to its great technological importance for semiconductor devices. LEED experiments^{2,3}, X-ray diffraction measurements^{4,7}, scanning tunneling microscopy (STM)⁵ and surface core-level photoelectron diffraction experiments⁶ find down to temperatures of 90K that on the Si(100) surface alternating buckled dimers in $p(2 \times 2)$ or $c(4 \times 2)$ structure are formed. These experimental findings are in agreement with those of various density functional calculations (DFT) applying the local density approximation (LDA) to a slab model of the surface^{11,13,16,18}. Applying the LDA to cluster models of this surface^{15,19} the energy difference between the buckled reconstruction and a reconstruction forming symmetric dimers is very small, so they can not draw a concluding result on the ground state structure. Earlier work done with semi-empirical quantum chemical methods⁸ favours the asymmetric reconstruction as a closed-shell Hartree-Fock treatment⁹ does. Including electronic correlations at the generalized valence bond level⁹ or within a configuration interaction (CI) approach¹⁴ yields a symmetrically dimerized ground state similar to the findings of unrestricted Hartree-Fock calculations¹⁰.

The wide spread density functional methods rely on the ground-state density and do not provide a many-body

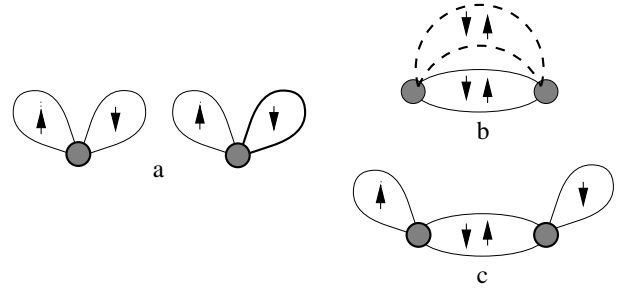


FIG. 1. The figures show sketches of the orbital structure of the ideal surface (a), and of a closed-shell (c) and open shell (b) structure of the reconstructed surface.

wave function. The electronic correlations are included implicitly only via the exchange-correlation functional. Regarding the process forming a dimer on the surface the question arises whether DFT can cope with bond breaking and bond formation. In the ideal Si(100) surface each surface atom has two singly occupied sp^3 hybrids (see Fig.1 a). In a simple-minded picture the surface energy is lowered by reducing the number of singly occupied orbitals. A bond is formed between two surface atoms yielding the (1×2) dimer structure. The nature of the bond can have two limiting cases: If a double-bond is generated between the two Si atoms (see Fig.1 b), this would lead to a closed-shell structure of the surface. Or, a single-bond is generated leaving on each surface atom a singly occupied orbital (see Fig.1 c). The true electronic structure of the surface can only be solved within a multi-determinant approach, which can describe all configurations between the two limiting cases. A second advantage of this approach is that the ideal and reconstructed surface are described at the same level of accuracy because we apply no restrictions on the wave function as single-reference approaches do. Up to now the multi-reference methods were applied to adsorption and diffusion processes of hydrogen on Si(100)²⁰. The most sophisticated correlation method applied to the reconstruction itself is by Jing and Whitten¹⁴ who made a two-determinant ansatz at the MCSCF level and perform a CI calculation using this reference.

We want to present a multi-reference self-consistent field (MCSCF) calculation for the ideal and reconstructed Si(100) surface to cope with the difficult bond structure. To deal with the dynamical correlations we supplement it with a multi-reference configuration interaction (MRCI) calculation. In addition we perform LDA and gradient corrected (GGA) density functional calculations for a direct comparison.

The paper is organized as follows: In Sec.II we present the multi-reference methods and provide the technical de-

tails. The resulting wave function is discussed in Sec.III. In Sec.IV we present the reconstruction energy, the geometry of the symmetric dimer and the question of dimer buckling. Conclusion follows in Sec.V.

II. MULTI-REFERENCE METHODS

Only closed-shell systems or high-spin open-shell system can be described within a single-determinant approach such as Hartree-Fock or single-reference configuration interaction (CI) methods to include correlations. In all other cases the suitable method is a multi-configuration self-consistent field (MCSCF) approach. The wave function is written as

$$|\Psi_{\text{MCSCF}}\rangle = \sum_I c_I |\Psi_I\rangle, \quad (1)$$

where $|\Psi_I\rangle$ is a determinant built up from molecular orbitals and c_I are the so-called CI-coefficients. The difference to a single-reference CI approach is that not only the CI-coefficients are optimized but also the coefficients of the orthonormal orbitals building up the $|\Psi_I\rangle$. Therefore the number of determinants involved in the MCSCF should be small compared with conventional CI. In the case of the Si(100) surface we select all possible determinants combining the four singly occupied sp^3 hybrids to a singlet. In addition we reoptimize the closed-shell orbitals of the first layer to account for the influence of the reconstruction on the bulk. The electronic correlations treated by a MCSCF ansatz are often called static correlations.

To describe the dynamical correlations we apply on top of the MCSCF a multi-reference configuration interaction (MRCI) with single and double excitations.

$$|\Psi_{\text{MRCI}}\rangle = \left(1 + \sum_{i\mu} \eta_i^\mu c_i^\dagger c_\mu + \sum_{ij\mu\nu} \eta_{ij}^{\mu\nu} c_i^\dagger c_j^\dagger c_\mu c_\nu \right) |\Psi_{\text{MCSCF}}\rangle \quad (2)$$

where μ and ν numbers the occupied orbitals and i and j the unoccupied ones. The coefficients η_i^μ and $\eta_{ij}^{\mu\nu}$ are determined variationally in the MRCI procedure. We restrict the dynamically correlated space to the surface orbitals.

We perform all calculations with the quantum-chemical program package MOLPRO94²¹, only for the DFT-calculations we use the latest version MOLPRO96²¹. The smallest possible cluster with one dimer is Si₉, the bulk-like bonds are saturated with 12 hydrogens. To test the influence of the bulk layers we perform calculations on Si₁₇H₂₀ and Si₃₁H₃₂, where the number of bulk layers increases. The Si—Si distance in the bulk is taken from experiment (2.352Å), the distance to the saturating hydrogen atoms is chosen equal to the one in SiH₄ (1.480Å).

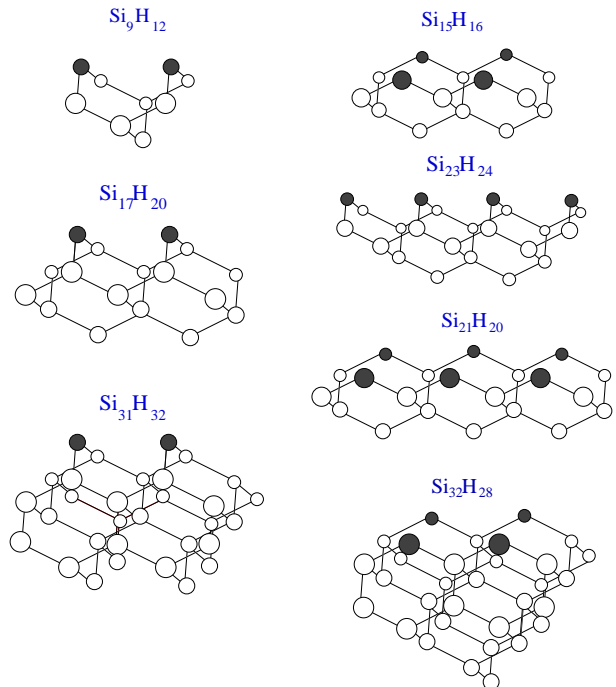


FIG. 2. The figure shows all Si_xH_y clusters which are used in the calculations; the surface atoms are shaded; the hydrogen atoms are not drawn.

In test calculations the geometry of the symmetric reconstruction is chosen such that all bonds have the bond length of the bulk. To test the interaction of the dimers we consider a Si₁₅H₁₆ cluster which contains two parallel dimers and Si₂₃H₂₄ which has two dimers in line. Additionally we used a Si₂₁H₂₀ cluster with three parallel dimers. The final results are obtained from Si₃₂H₂₈, which simulates six bulk layers and two dimers. All clusters are shown in Fig. 2.

We apply a 4-valence-electron scalar-relativistic energy-consistent pseudopotential for Si²² with the corresponding valence basis set²². It is supplemented by various sets of polarization functions, which are optimized by performing correlated calculations for the free atom. For hydrogen we apply a minimal basis consisting of the fully contracted 1s functions of Dunning²³.

III. MANY-BODY WAVE-FUNCTION OF THE IDEAL AND RECONSTRUCTED SURFACE

For the ideal surface we perform a high-spin ($S = 2$) single-determinant Hartree-Fock calculation to generate the starting orbitals for the MCSCF calculation in which the four singly occupied orbitals in the active space are combined to a singlet ground-state. In addition the closed-shell orbitals of the first bulk layer are reoptimized. One way to discuss the resulting orbitals is to calculate the natural orbitals which diagonalize the density matrix (see Table I). We find three quite close-lying orbitals two of which have binding and one has antibind-

TABLE I. The mean occupation number of the natural orbitals and their binding character is shown both for the ideal and reconstructed surface.

	character	\bar{n}
ideal	1. bind.	1.52
	2. bind.	1.06
	3. antib.	0.94
	4. antib.	0.48
sym. reconstr.	1. bind.	1.98
	2. bind.	1.63
	3. antib.	0.37
	4. antib.	0.02

ing character. Even the second antibinding one has a mean occupation of half an electron. Regarding the coefficients of the MCSCF expansion there are ten configurations with a coefficient greater than 0.1. This shows clearly that the ideal surface can not be described within a single-determinant approach. The singlet closed-shell HF energy lies about 1 eV higher in energy than the corresponding MCSCF value.

For the symmetric reconstructed surface we start the MCSCF calculation with the orbitals of a triplet HF determinant. But the active space of the MCSCF calculation is exactly the same as in the ideal case. The natural orbitals look quite different. A low-lying binding orbital is doubly occupied forming a single bond between the surface atoms. A second binding orbital is occupied with 1.6 electrons. A double occupancy of this orbital would correspond to a double-bond between the surface atoms. The significant population of the first antibinding orbital with 0.4 electrons contradicts the closed-shell picture. The MCSCF expansion is dominated by the configuration where the two binding orbitals are occupied, but the occupation of the first antibinding orbital is not negligible. In a single-determinant description the triplet state would be energetically favoured by 0.9 eV leading to an unphysical ferromagnetic surface. In the MCSCF calculation the triplet state is about 0.3 eV higher in energy than the singlet ground state.

In both cases, i.e., in the ideal and in the symmetrically reconstructed surface we find a singlet ground state which can be only described within a multi-configuration approach. Through this we can provide for both cases an adequate description. So we can compare the ground-state energies of the two structures yielding the reconstruction energy.

IV. RESULTS AND DISCUSSION

A. Basis set dependence

In a first step we want to test the quality of the basis set used. We calculate the reconstruction energy on the MCSCF and MRCI level for the Si_9H_{12} cluster. Al-

TABLE II. Influence of the atomic basis set on the reconstruction energy at different correlation levels. The calculations are performed in the Si_9H_{12} cluster.

basis	$\Delta E_{\text{MCSCF}}[\text{eV}]$	$\Delta E_{\text{MRCI}}[\text{eV}]$
[2s2p]	0.90	1.08
red. basis	1.17	1.54
[2s2p]1d	1.26	1.56
(4s4p)1d	1.27	1.59
[3s3p]2d	1.29	1.60
[3s3p]2d1f	1.33	1.73
(4s4p)3d2f1g	1.34	1.73

though the question of the basis is a technical one, it is possible to draw some physical conclusions.

The default basis is of valence-double- ζ quality (4s4p)/[2s2p] supplemented by one d polarization function with exponent 0.4. In Table II the results are listed. Calculating the reconstruction energy without any d -function yields only 70% of the value with the default basis. Applying a d -function only for the surface and the first layer atoms (reduced basis) we determine 93% of the default MCSCF energy and 97% of the default MRCI energy. The better value of the MRCI is clear, because in this calculation only the surface orbitals are involved, whereas in the MCSCF the first layer is re-optimized, too. This basis set will be our choice for the larger clusters. The increase of the reconstruction energy when supplementing a d polarisation function indicates the important role of the electronic correlations on the formation of the bond in the dimer. Uncontracting totally the valence basis set yields only a small increase in the reconstruction energy. This shows that the [2s2p] basis is of equal quality for both geometries. The same holds true if we split the d -exponent into two (0.23, 0.8). To receive a balanced basis we uncontract the valence basis to [3s3p]. Applying an additional f -function (exponent 0.35) the reconstruction energy rises by 6% on the MCSCF level and by 10% on the MRCI level. This indicates that to correlate the π -bond the f -function is more important in the reconstructed geometry, especially for the dynamical correlation covered by the MRCI. Uncontracting the valence basis set totally to (4s4p) and adding a (3d2f1g) polarization set (exponents from Ref.[24]) yields nearly no changes (smaller than 1%) on the reconstruction energy on the MCSCF and MRCI level. This indicates that the basis set limit is reached for the reconstruction energy.

B. Influence of bulk layers

To check the influence of the bulk layers on the surface reconstruction we perform MCSCF and MRCI calculations for three different clusters using the reduced basis. Si_9H_{12} simulates three bulk layers, $\text{Si}_{17}\text{H}_{20}$ four layers and $\text{Si}_{31}\text{H}_{32}$ five layers whereas all have one sur-

TABLE III. Influence of the bulk layers on the reconstruction energy at different correlation levels. The calculations are performed in the reduced basis.

cluster	$\Delta E_{\text{MCSCF}}[\text{eV}]$	$\Delta E_{\text{MRCI}}[\text{eV}]$
Si ₉ H ₁₂	1.17	1.54
Si ₁₇ H ₂₀	1.33	1.67
Si ₃₁ H ₃₂	1.30	1.61

TABLE IV. Influence of the dimer interaction on the reconstruction energy at different correlation levels. The calculations are performed in the reduced basis.

cluster	$\Delta E_{\text{MCSCF}}[\text{eV}]$	$\Delta E_{\text{MRCI}}[\text{eV}]$	$\Delta E_{\text{LDA}}[\text{eV}]$	$\Delta E_{\text{GGA}}[\text{eV}]$
Si ₉ H ₁₂	1.17	1.54	2.01	1.43
Si ₁₅ H ₁₆	1.15	1.46	1.85	1.27
Si ₂₁ H ₂₀	1.13	—	1.76	1.27
Si ₂₃ H ₂₄	1.15	1.46	—	—

face dimer; for results see Table III. The changes between three and four layers are quite significant, i.e. up to 14% of the reconstruction energy at the MCSCF level. This shows that the Si₉H₁₂ cluster is not fully reliable for describing the surface. The difference between four and five layers is up to 4% and is tolerable for the determination of the reconstruction energy. But in our opinion it is not possible to calculate reliable relaxed distances of the bulk atoms, which is a shortcoming of the cluster approach. Experimentally it is proven⁷ that there are relaxations up to the fifth bulk layer.

C. Interaction of dimers

Although we have checked in the last section, that the 3-layer clusters can not fully describe the surface reconstruction we select four different 3-layer clusters in order to test the interaction of the dimers. Si₉H₁₂ has one dimer, Si₁₅H₁₆ has two parallel dimers and Si₂₁H₂₀ has three. Si₂₃H₂₄ has two dimers in line. Concerning the reconstruction energy on the MCSCF level, all selected clusters differ by at most 4% concluding that the interaction on the MCSCF level is weak (see Table IV). On the MRCI level we calculate only the cluster with one and two parallel dimers. The difference is larger than at the MCSCF level indicating that the dynamical correlations are more important for the dimer interaction than are the static correlations.

Treating the clusters in a LDA approach (Slater-Dirac exchange²⁵ and Vosko-Wilk-Nusair correlation functional²⁶) the interaction between the dimers is larger by up to 12%. This can be understood from the wave function structure resulting from the LDA. If more than one dimer exist, there is an energy gain due to delocalization of the surface electrons. In a gradient corrected density functional approach (GGA, Becke exchange²⁷ and Lee-Yang-Parr correlation functional²⁸) we found a sim-

ilar behaviour, but there the effect of delocalization is smaller than in the LDA and occurs only between two dimers. This delocalization energy is larger on the ideal surface than on the reconstructed surface due to the close lying and therefore well mixing states. This results in an overestimation of the dimer interaction on the LDA level. If the surface is treated on the MCSCF level the mixing between different states can occur within one dimer, so that both ideal and reconstructed surface are treated at the same level of accuracy.

D. Surface reconstruction energy — comparison of different methods

Combining the results of the previous sections we select the Si₃₂H₂₈ cluster for our final calculation. This cluster has two dimers and the bulk is modelled up to the sixth bulk layer. Due to the quite large size of the cluster we can treat it only with the reduced basis. The surface reconstruction energy at the MCSCF level is 1.13 eV. Including dynamical correlations yields an increase of nearly 40% resulting in 1.56 eV. Concerning the limited basis used in this calculation we can estimate based on our basis set test calculations a final value of 1.75 eV. The error due to the cluster size is estimated to be by $\pm 5\%$. Comparing our result with various LDA-slab calculations (Dabrowski et al.¹³ 1.5 eV; Fritsch et al.¹⁶ 1.51 eV; Ramstad et al.¹⁸ 1.8 eV; Roberts et al.¹¹ 2.02 eV) the agreement is remarkably good. In order to compare the results of different methods in more detail we apply the different methods to the same cluster with the same basis set. We choose again the Si₉H₁₂ cluster using the $[2s2p]1d$ basis. DFT methods are applied with two different exchange correlation functions. The LDA described above yield a reconstruction energy of 2.01 eV which is nearly 30% above the MRCI value of 1.56 eV. This value is certainly lowered due to dimer interaction as described in the previous section. Using the GGA approach the reconstruction energy (1.43 eV) is underestimated by 8%. The DFT treatments yield a singlet ground state for the reconstructed surface in contradiction to a single-determinant Hartree-Fock calculation, but the reconstruction energy is dependent on the chosen functional. The results show the known feature that LDA overestimates binding whereas the GGA gives a substantial improvement.

E. Geometry of the symmetric reconstruction

We argued in the previous sections that the clusters are too small for treating the relaxations of the bulk layers due to surface reconstruction. But it is reasonable to optimize the dimer bond length (b_{dimer}) and the bond length of the surface atoms to the first layer atoms ($b_{1.\text{layer}}$); for results see Table V. To check the

TABLE V. Optimized dimer bond length and first layer bond length of the symmetric reconstructed surface.

method		$b_{\text{dimer}}[\text{\AA}]$	$b_{1,\text{layer}}[\text{\AA}]$
MCSCF	Si_9H_{12}	2.41	2.36
MRCI	Si_9H_{12}	2.37	2.36
MCSCF	$\text{Si}_{17}\text{H}_{20}$	2.40	2.36
MRCI	$\text{Si}_{17}\text{H}_{20}$	2.35	2.36
LDA	[11]	2.23	2.29
	[18]	2.23	2.27
	[16]	2.26	2.31

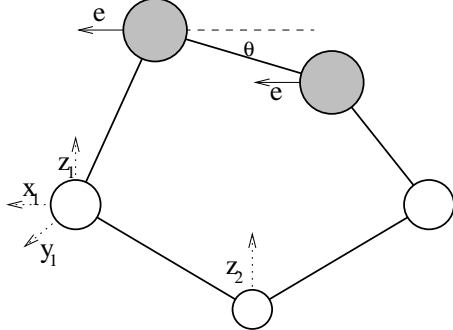


FIG. 3. The figure shows a projection of the Si_9H_{12} cluster where the displacements concerned for the asymmetric buckling are indicated.

cluster-size dependence we perform the calculations for the Si_9H_{12} cluster as well as for the $\text{Si}_{17}\text{H}_{20}$ cluster within the $[2s2p]1d$ basis. The results show, that the bond lengths are only slightly cluster dependent. The changes are less than 0.02\AA . The dynamical correlations reduce the dimer bond length by about 2%. Compared with the dimer bond-length of the asymmetric dimer from different experiments (Bullock et al.⁶ 2.25\AA ; Jedrecy et al.⁴ 2.32\AA ; Aono et al.¹ $2.4\pm 0.1\text{\AA}$; Holland et al.³ 2.47\AA ; Yang et al.² 2.54\AA ; Felici et al.⁷ 2.67\AA) we agree quite well with the second and third measurement. LDA-slab calculations (see Table V) yield a dimer bond length quite below the bulk value.

F. Asymmetric reconstruction

In this section we want to arise the question of the dimer buckling. Up to now we allowed only for the symmetric reconstruction which maintains the local C_{2v} -symmetry. We test the buckling by lowering the symmetry in the Si_9H_{12} cluster with the $[2s2p]1d$ basis. We allow for a buckling angle Θ and a displacement of the dimer parallel to the surface (see Fig. 3). The dimer bond length is fixed to the value obtained in the optimization of the symmetric case. In the MCSCF and MRCI treatment the symmetric dimer has the lowest energy contrary to the DFT calculations where we find a buckling of 9° in LDA and of 8° in GGA. The energy gain is very small, i.e., 0.031 eV in LDA and 0.014 eV in

GGA. From this we can conclude that the used approximations to DFT overestimate the electronic contribution to the buckling due to an overestimation of the closed-shell structure.

The experimentally observed buckling could be driven by relaxation of the bulk atoms. Although the Si_9H_{12} cluster is quite small to resolve relaxations we performed some test calculations within this model. We allow for the first bulk layer atoms to relax in all directions, whereas we regard for the second bulk layer only a relaxation perpendicular to the surface (see Fig. 3). On the MCSCF level, where all orbitals are reoptimized we do not find any buckling although there is a significant relaxation of the first bulk layer atoms in the dimer direction of about 0.08\AA and of the second bulk layer atoms perpendicular to the surface of about 0.09\AA . The other relaxations are smaller by about one order of magnitude. From this we can conclude that in our cluster model the bulk relaxations do not drive the asymmetric buckling.

To account for the dimer interaction we regard the $\text{Si}_{15}\text{H}_{16}$ cluster with two dimers. We model the asymmetric $p(1\times 2)$ structure as well as the $p(2\times 2)$ structure with alternating buckled dimers. For fixed buckling angle the $p(2\times 2)$ structure is lower in energy than the asymmetric $p(1\times 2)$ structure, e.g., for an angle of 2° by 0.018 eV per dimer and for an angle of 10° by 0.060 eV . But still the symmetric dimer is lowest in energy, also if we allow for the relaxations we determined in the Si_9H_{12} cluster. This shows that the interaction of two dimers is not enough to stabilize a buckled structure. This is in contradiction to the LDA cluster results from Yang et al.¹⁹ who find a stable $p(2\times 2)$ structure in the $\text{Si}_{15}\text{H}_{16}$ cluster.

Our finding of a symmetric ground state is in agreement with all previous correlation calculations, which show that the proper treatment of the electronic correlations stabilize the symmetric reconstruction. We can exclude an asymmetric $p(1\times 2)$ structure, which LDA slab calculations^{11,13,16,18} find about 0.1 eV more stable than the symmetric one. As we can only calculate the interaction of two dimers, there is the possibility that the interaction of many dimers can yield a buckled ground state. But regarding the STM experiment of Badt et al.⁵, who find a buckled $c(2\times 4)$ structure at 90 K , they claim that the buckling can be induced by a defect or a step at the surface. The defect-free surface is difficult to prepare, so the question of buckling of the $\text{Si}(100)$ surface is experimentally still not solved.

To address the question of metallicity of the symmetric reconstructed $\text{Si}(100)$ surface, which is found in various DFT calculations and discussed in detail in Ref.[29], in a many-body description as applied here there can exist a gap due to electronic correlations in the symmetric reconstruction, too. But in principle the question of metallicity cannot be solved in a cluster approach.

V. CONCLUSION

We have performed MCSCF calculations for the ideal and reconstructed Si(100) surface. In both cases the many-body ground state is a singlet, but it can only be described by several determinants. On the reconstructed surface a dimer is formed. The bond structure is a mixture between a double-bond and a single-bond with two singly occupied orbitals. To account for the dynamical correlations we apply on top of the MCSCF result a MRCI calculation. Determining the reconstruction energy we find good agreement with various LDA slab calculations. The dimer bond length agrees better with experiment than the LDA one. The asymmetric reconstruction is overestimated in the LDA while our fully correlated treatment finds the symmetric dimer more stable regarding the electronic structure of one dimer and relaxations of the bulk atoms. The buckling observed in experiment can be due to a small concentration of defects on the Si(100) surface. It is possible that an alternating buckled structure is induced by defects and persist down to low temperatures due to dimer interactions.

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